

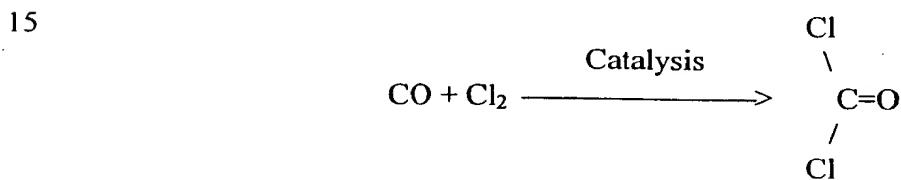
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a. Phosgene Having Low Content of Carbon Tetrachloride  
Phosgene which is low in carbon tetrachloride

This invention relates to phosgene which is low in carbon tetrachloride, to a process for the production thereof, and to the use thereof for producing polycarbonates and polyester 5 carbonates.

Phosgene is an important starting material for producing intermediates and final products in many branches of chemistry, particularly for the production of isocyanates, polycarbonate plastics and esters of chloroformic acid. Pure phosgene is a colourless, 10 toxic gas which is susceptible to hydrolysis. Under normal pressure it boils at -127.8°C and condenses at 7.56°C to form a colourless liquid.

It is known that phosgene can be produced by the catalytic combination of carbon monoxide (CO) and elemental chlorine (Cl<sub>2</sub>):



Activated carbon is mostly used as the catalyst. The reaction is exothermic and the conversion is almost complete. The reaction is usually conducted in tubular reactors which are made from standard steel or stainless steel and which are packed with catalyst. 25 These tubes are generally cooled externally in order to dissipate the heat of reaction. Depending on the processing conditions, the phosgene which is produced by this process contains varying amounts of carbon tetrachloride (CCl<sub>4</sub>) as an impurity. This is formed by unwanted secondary reactions such as disproportionation reactions, excessive chlorination of the carbon monoxide, chlorination of the carbon catalyst and chlorination 30 of methane (CH<sub>4</sub>). The degree of contamination by carbon tetrachloride of phosgene which is produced by commonly-used processes usually falls within the range from 250 to 2000 ppm.

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The formation of carbon tetrachloride as a by-product during the production of phosgene is problematical from many aspects. Thus, due to the environmental harmfulness of chlorinated hydrocarbons, costly precautions have to be taken to ensure that the carbon tetrachloride formed in the reactions is not discharged into the environment. Moreover, even slight contents of carbon tetrachloride have a disadvantageous effect on some products which are manufactured from phosgene, particularly plastics. For example, high-purity phosgene with a carbon tetrachloride content of 250 ppm at most is required for the production of polycarbonate plastics, in order to prevent discolouration of the final product, which is normally colourless and transparent.

JP 88-156040 describes a process for producing phosgene which is low in carbon tetrachloride by the reaction of carbon monoxide with chlorine over activated carbon at 350°C, whercin the activated carbon catalyst is purified before reaction by treatment with acid to remove impurities such as transition metals, boron, aluminium and silicon. The phosgene which is produced by this process has a carbon tetrachloride content of 150 ppm. A disadvantage of this process, however, is the costly pretreatment of the activated carbon catalyst.

JP 80-014044 proposes a reactor for the conversion of chlorine and carbon monoxide into phosgene, in which the activated carbon catalyst is positioned at the reactor walls with the aid of a metal mesh. This arrangement prevents overheating of the catalyst bed. The phosgene which is produced in a reactor such as this at temperatures of 200 to 250°C and at a throughput of 600 to 1200 l/h has a carbon tetrachloride content of 250 to 400 ppm. A disadvantage of this process, however, is that repacking the reactor with activated carbon when the activity of the latter decreases is more expensive than is the operation of conventional tubular reactors.

The underlying object of the present invention is to provide phosgene with an even lower carbon tetrachloride content.

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This object is achieved by a grade of phosgene which contains less than the 150 ppm of carbon tetrachloride. The present invention further relates to a process for producing a grade of phosgene such as this by the reaction of carbon monoxide with chlorine in the presence of elemental carbon at a temperature of 30 to 80°C and at a pressure of 120 to 5 400 kPa<sub>abs</sub>, as measured directly downstream of the phosgene generator.

It is advantageously possible to conduct the process according to the invention in customary tubular reactors made of standard steel or stainless steel, the tubes of which are packed with the carbon catalyst. The tubular reactor can be operated continuously or 10 batch-wise.

Carbon tetrachloride and chlorine are introduced into the reactor in approximately equal parts, preferably at room temperature. To ensure that all the chlorine is reacted, a slight excess of carbon monoxide can be used. Before they enter the reactor, the two reactants 15 are preferably mixed in a suitable mixing device, in a static mixer for example.

Another advantage of the process according to the invention is that no special preparation of the catalyst is necessary.

20 The temperature of the gas stream emerging from the reactor should not exceed 70 to 80°C, as measured directly downstream of phosgene generator. The temperature of the gas stream emerging from the reactor in the process according to the invention is preferably 40 to 70°C. The gas stream is prevented from exceeding these temperatures with the aid of appropriate cooling devices which dissipate the heat of reaction which is 25 released during the reaction and which prevent any overheating of the catalyst.

Activated carbon is preferably used as the carbon catalyst. Granular activated carbon with a grain diameter of 3 to 4 mm is preferably used as the catalyst. The pore surface area of the activated carbon is preferably about 1000 m<sup>2</sup>/g. The apparent density of the 30 activated carbon used is preferably about 450 g/l.

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The pressure which is measured directly downstream of the phosgene reactor is preferably 300 kPa<sub>abs</sub>. at most. It is thereby ensured that phosgene cannot condense in the reactor.

5 The phosgene which is produced by the process according to the invention and which emerges from the top of the reactor is preferably condensed at temperatures of -10 to -20°C. Due to its low carbon tetrachloride content of less than 150 ppm, it can be used directly, without further purification, for producing polymers comprising a carbonate bond, particularly polycarbonates or polyester carbonates.

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The chlorine which is used in the reaction can be produced by customary industrial processes such as chlor-alkali electrolysis or hydrogen chloride electrolysis, and should be as pure as possible. Chlorine with a degree of purity higher than 98 % is particularly suitable. Liquid chlorine from a storage vessel is preferably used. This is evaporated in a 15 heated gasifier and is subsequently freed from any entrained liquid chlorine in a re-evaporator.

20 The carbon monoxide which is used in the reaction can be produced by customary methods, for example from natural gas/naphtha in a synthesis gas installation or by blowing coke with oxygen. It has proved to be particularly advantageous if the carbon monoxide has a methane content of less than 50 ppm.

The invention is explained in more detail below by means of examples.

**Example 1**

500 Nm<sup>3</sup>/h carbon monoxide with a purity of 97.5 % and a methane content of 50 ppm as determined by on-line IR measurement (Method 2301-0207901-91D), and 480 Nm<sup>3</sup>/h 5 chlorine with a purity of 99.9 % were mixed at room temperature and were fed to a phosgene generator packed with activated carbon (grain diameter about 4 mm, pore surface area about 1000 m<sup>2</sup>/g, apparent density about 450 g/l). The generator was cooled so that the temperature of the phosgene formed, as measured directly after the phosgene left the generator, was 55°C. The pressure as measured directly after the phosgene left 10 the generator was 80 kPa<sub>gauge</sub> (180 kPa<sub>abs</sub>). The phosgene produced had a carbon tetrachloride content of 100 ppm.

**Example 2**

15 500 Nm<sup>3</sup>/h carbon monoxide with a purity of 98 % and a methane content of 50 ppm as determined by on-line IR measurement (Method 2301-0207901-91D), and 480 Nm<sup>3</sup>/h chlorine were mixed at room temperature and were fed to a phosgene generator packed with activated carbon (grain diameter about 4 mm, pore surface area about 1000 m<sup>2</sup>/g, apparent density about 450 g/l). The generator was cooled so that the temperature of the 20 phosgene formed, as measured directly after the phosgene left the generator, was 40°C. The pressure as measured directly after the phosgene left the generator was 40 kPa<sub>gauge</sub> (140 kPa<sub>abs</sub>). The phosgene produced had a carbon tetrachloride content of 80 ppm.

**Comparative example**

25 500 Nm<sup>3</sup>/h carbon monoxide with a purity of 98% and a methane content of 10 ppm were mixed at room temperature with 485 Nm<sup>3</sup>/h chlorine and were fed to a phosgene generator as in Examples 1 and 2. The generator was cooled so that the temperature of the phosgene formed, as measured directly after it left the generator, was 85°C. The 30 pressure, which was likewise measured directly after the phosgene left the generator, was 600 kPa<sub>gauge</sub> (700 kPa<sub>abs</sub>). The phosgene produced had a carbon tetrachloride content of 290 ppm.